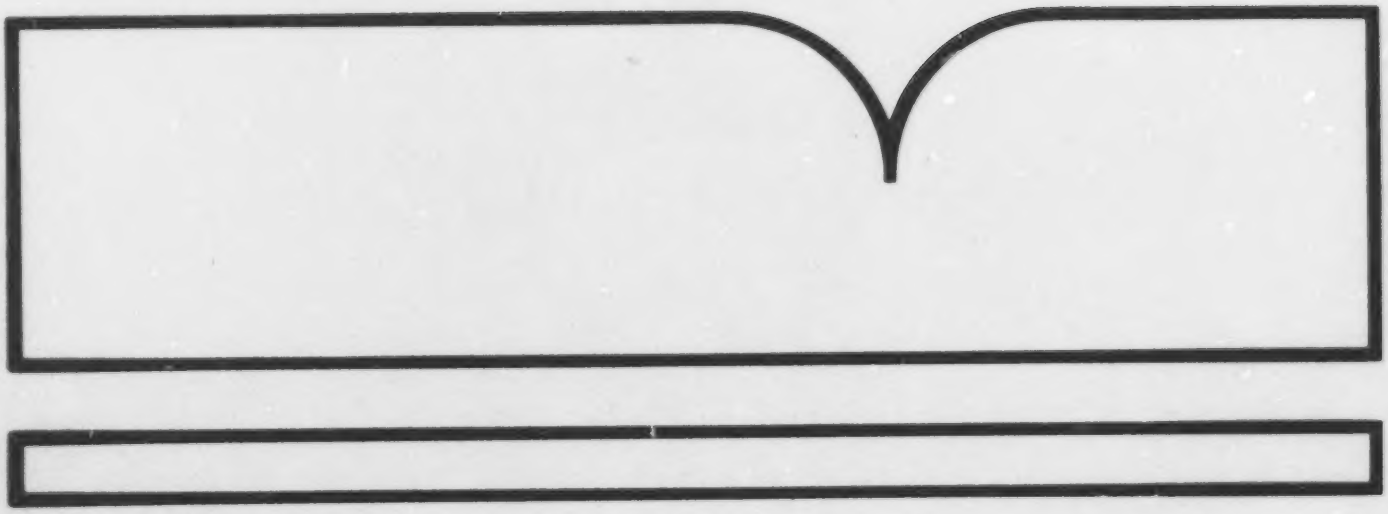
PB86-189446

Unit Operations Approach in Exposure/Release Evaluation for New Chemicals

(U.S.) Environmental Protection Agency
Cincinnati, OH

Apr 86



U.S. Department of Commerce
National Technical Information Service
NTIS

PB86-189446

EPA/600/D-86/089
April 1986

UNIT OPERATIONS APPROACH IN EXPOSURE/RELEASE EVALUATION FOR NEW CHEMICALS

by:

Kin F. Wong, Ph.D.
Office of Toxic Substances
U.S. Environmental Protection Agency
401 M. Street, S.W.
Washington, D.C. 20460

and

M. Lynn Apel
Office of Research and Development
U.S. Environmental Protection Agency
26 W. St. Clair Street
Cincinnati, Ohio 45268

WATER ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OH 45268

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/D-86/089	2.
3. RECIPIENT'S ACCESSION NO. PB86 189446/AS	
4. TITLE AND SUBTITLE "Unit Operations Approach In Exposure/Release Evaluation For New Chemicals"	5. REPORT DATE April 1986
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Kin F. Wong and M. Lynn Apel	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Environmental Protection Agency Office of Toxic Substances/Office of Res. and Devel. 401 M. Street 26 W. St. Clair Street Washington, D.C. 20460 Cincinnati, Ohio 45268	10. PROGRAM ELEMENT NO. P.E.# CCTLIA
	11. CONTRACT/GRANT NO. N/A - Inhouse Paper
12. SPONSORING AGENCY NAME AND ADDRESS Water Engineering Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268	13. TYPE OF REPORT AND PERIOD COVERED ASCE NCEE Conference Paper
	14. SPONSORING AGENCY CODE EPA/600/14
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

Recognizing the potential problems associated with the proliferation of new chemicals, Congress passed the Toxic Substances Control Act (PL94-469) (TSCA) in 1976. This Act establishes EPA's authority to regulate, if necessary, all commerical chemicals before they are commercialized. Effective July 1, 1979, section 5 of TSCA requires persons to notify EPA through the submission of a Premanufacturing Notice (PMN) at least ninety days before the manufacture or import of a chemical not on the "Inventory" of existing chemical substances.

Since a new "PMN chemical" has not been commercialized, potential exposures and releases resulting from the manufacture, processing and/or use of the chemical must be estimated based on minimum data. The concept of "unit operations" has been proposed for the evaluation of such potentials. Predictive models are being developed to identify possible sources of chemical releases and points of potential worker exposure from several unit operations. Input variables for these models include the physical properties of the chemical substance and the operational specifications of the unit operation.

The application of the concept has been discussed in several examples. Further research is in progress using simulated and field studies to improve these models.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Exposure Chemical Release Industrial Hygiene Inhalation Dermal	Unit Operations Unit Processed Occupational Exposure	

18. DISTRIBUTION STATEMENT Release Unlimited	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 11
	20. SECURITY CLASS (This page) Unclassified	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

UNIT OPERATIONS APPROACH IN EXPOSURE/RELEASE EVALUATION FOR NEW CHEMICALS

Kin F. Wong, Ph.D.[1]
M. Lynn Apel, M. ASCE[2]

INTRODUCTION

Recognizing the potential problems associated with the proliferation of new chemicals and their widespread applications, Congress passed the Toxic Substances Control Act (PL94-969) [TSCA] in 1976. TSCA requires industry to notify the Environmental Protection Agency (EPA) before commercialization of a new chemical substance or the development of a "significant new use" of an existing chemical. EPA is empowered to require testing, to issue a limitation or ban, or to regulate the use of the chemical substance if it is determined that a new chemical, or new use of an existing chemical, poses any unreasonable risk to human health or the environment.

Effective July 1, 1979, section 5 of TSCA requires persons to notify EPA through the submission of a Premanufacture Notice (PMN) at least ninety days before manufacturing or importing a new chemical substance for commercial purposes. A new chemical substance as defined in the Act is any chemical substance that is not included on the list or "Inventory"* of existing chemical substances compiled by EPA under TSCA, section 8(b), in 1979.

Information that PMN submitters must provide includes (1) test data in their possession or control; (2) descriptions of health and environmental effects data that they know or can reasonably ascertain; and (3) known or reasonably ascertainable information on chemical identity; proposed categories or use; proposed volume production; byproducts resulting from manufacture, processing, use, or disposal; the amount of new chemical released to the environment; workplace exposure; and manner or method of disposal (48 FR 21722).

Once EPA receives a section 5 notice, the Agency has ninety days to review it, unless for good cause EPA extends the review period for up to an additional ninety days. During the review period, EPA may act to regulate the production or use of the new chemical substance, prohibit or limit the manufacture (including import), processing, distribution in commerce, use, or disposal of a new chemical substance until information sufficient to evaluate its health and environmental

*Toxic Substances Control Act Chemical Substances Inventory

[1]Office of Toxic Substances, U. S. Environmental Protection Agency, Washington, D. C. 20460
[2]Office of Research and Development, U. S. Environmental Protection Agency, Cincinnati, Ohio 45268

effects is provided. EPA may also regulate a new chemical substance if it finds that there is a reasonable basis to conclude that the manufacture, processing, distribution, use, or disposal of the substance will present an unreasonable risk of injury to human health or the environment. If no action is taken by EPA during the review period, a substance can enter commercial production unregulated under TSCA. As a result, section 5 of the Act does not establish a registration program, and EPA has not in any sense "approved" substances that have passed through review without regulation.

From commencement of the notice review program on July 1, 1979 to September 1983, EPA received 3,012 valid PMN's. Of the total number, the review period had expired on 1,878 and 777 had entered commercial production. During this period, EPA issued fourteen orders regulating the production of twenty-seven new chemical substances pending the development of additional data (USEPA, 1984). Since this time, approximately 1300 to 1400 PMN's per year have been submitted to the Agency for review in 1984.

EXPOSURE/RELEASE ASSESSMENT

A number of factors are considered by EPA in it's review of PMN submissions. These factors include the potential toxicity of the substance, and the potential for humans and the environment to be exposed to the substance during its manufacture, processing, use and disposal. This presents a tremendous challenge for the Agency. Since a new chemical has not been commercially produced, often very little exposure or release data are available. Frequently physical property data are also limited (OTA 1983). In addition, the new chemicals reviewed through the PMN process reflect the diversity of the 40,000 to 50,000 chemicals in the current Chemical Substances Inventory. The large number of new chemicals, approximately 1500 each year, and the diverse chemical families and uses make the problem almost insurmountable since the entire review process must take less than ninety days. The situation is somewhat similar to what the engineering profession faced in the early days in designing an educational framework for training new engineers who would be well grounded in the basic principles, but yet would be readily adaptable to a carrer in a variety of industries.

The concept of unit operations and processes was developed to meet the demand for organizing the practice of chemical engineering such that it could be adaptable to a large number of products and industries. It has been successfully utilized over the years to provide a unified treatment on operations in the chemical processing and allied industries (Groggins 1935, Reynolds 1984, Perry, 1963).

The same approach may also be applied to the estimation of potential exposure and release of toxic materials from the manufacture and/or processing of new chemicals. By characterizing a fundamental set of unit operations and processes in a representative cross-section of industrial segments, data bases and predictive models may be established which can be extrapolated to new chemicals and processes. In order to include all activities of concern to the PMN

program, the classical set of unit operations and processes has to be expanded to cover areas such as sampling, cleaning and maintenance as well as downstream operations such as extrusion, spray-coating and electroplating.

Since 1981 EPA has sponsored several studies to develop this approach into a viable tool for use in PMN review. Early on the research program focused on literature surveys of mathematical models and exposure/release information on many unit operations and processes listed in Table 1 (Bomberger et al., 1983, Clement Associates 1981, JACA 1985, MITRE 1985). Subsequent efforts led to the development of a set of simple models for rapid estimation of potential workplace exposure and releases (Berman 1982, USEPA 1985) and more in-depth studies and modeling on drumming and bagging operations (MRI 1985). As a result of this research program EPA currently has at its disposal a variety of methodologies for assessing potential workplace exposure and release for a new chemical when only minimal data are available. Although many of the basic elements are rudimentary in nature, they are based on some theory and data presently available. A few examples are shown below to illustrate the variety of approaches used.

TABLE 1

LIST OF UNIT OPERATIONS AND UNIT PROCESSES CONSIDERED

UNIT OPERATIONS	UNIT PROCESSES
Filtration	Alkylation
Drying	Halogenation
Size Reduction	Hydrohalogenation
Mixing	Polymerization
Process Sampling	Diazotization
Packaging	Coupling
Maintenance	Amination
Clean-up	Phosgenation
Centrifugation	Nitration
Unloading	Oxidation/Reduction
Electroplating	Pyrolysis
Extrusion	
Spray-coating	
Extraction	Esterification
Flaking	Carbonylation
Agglomeration	Dehydrohalogenation
	Sulfonation & Sulfation
Distillation	Condensation
Flotation	Catalytic cracking
Absorption	Dehydrogenation
Solids transfer	Electrolysis
Decanting	Hydrolysis
Adsorption	Hydrogenation
Osmosis	Dehydration

Example 1. Inhalation Exposure in Drumming of Liquids

Drumming is a common activity associated with the manufacture and processing of many chemicals. A simple mass balance model was developed to account for inhalation exposure during drumming (Berman 1982). Inhalation exposure to a substance may be estimated from a knowledge of its airborne concentration and the respiratory rate (USEPA 1985).

The simplest model is to consider the work area as an enclosed box whereby the substance is being released continuously to the atmosphere from a source and that it is also constantly removed by ventilation. For simplicity, let us assume that there is no depletion of the substance due to chemical reaction (degradation). A material balance will yield an equation given in many industrial hygiene and engineering texts (e.g. Harris and Arp 1979) relating the equilibrium concentration to the generation rate and ventilation:

$$C = G/kQ$$

where C is the equilibrium concentration of the substance in air, G is the generation rate, k is the mixing factor and Q is the ventilation rate. Thus the estimation of inhalation exposure reduces to an exercise in estimation of the generation rate. Several common exposure scenarios were constructed with the generation rate expressions (Berman 1982). For vapor generation from drumming, the filling rate is assumed to be fast compared to evaporation so that the main contribution to generation is given by the displacement of vapor from the filling action. By assuming ideal gas behavior the volume of vapor displaced is given by

$$G = MpVr/RT$$

where M is the molecular weight, p is the vapor pressure, V is the volume of the drum, r is the filling rate in drums per time, R is the gas constant and T is the temperature during filling.

Example 2. Dermal Exposure in Cleaning Equipment

Cleaning of equipment is another major unit operation encountered in many processes. Dermal exposure involves two regimes.

For situations where absorption is fast the limiting factor is the amount of chemical available at the skin surface. By postulating a liquid film thickness the amount of chemical may be estimated from the density and the skin area. Experimental measurements by several authors have been made to characterize film thickness (Weaver 1978, Versar 1984, Wong 1982). Results indicated a range of 0.01mm to 0.1mm for the liquids studied. The dermal exposure per contact is then given by

$$\text{Exposure} = CdAh$$

where C is the concentration of the substance of concern in the bulk liquid, d is the density of the liquid, A is the area of the skin surface, and h is the thickness of the liquid film. The total dermal exposure can be calculated by assuming an appropriate number of contacts.

For situations where absorption is slow, the dermal exposure is governed by the rate of material transport across the skin surface. This approach has been applied to the estimation of dermal exposure to N-nitrosodiethanolamine (Wong 1984). Permeation data were based on measurements using excised human skin. The dermal exposure is given by

$$\text{Dermal exposure} = (Kp)CAt$$

where Kp is the permeability constant in cm/hr and t is the elapsed time. To use the model, the duration of exposure is estimated rather than the number of contacts.

Example 3. Release Estimate for Phase Separations

Phase separation is a common unit operation whereby a waste stream is produced. To estimate the amount of substance released to the environment a knowledge of the partition properties is necessary. Assuming phase equilibrium, the principles of thermodynamics tell us that the concentration of substance x in each of the two phases is related by the equality of chemical potential or activities.

$$Kd = x/x'$$

where x and x' are the mole fraction of the substance in the two phases, Kd is the distribution coefficient relating the distribution of the substance in the two phases. Methods exist in the literature for calculation of Kd from activity coefficient data (Lyman et al., 1982, Perry 1963), while x may be calculated from a knowledge of the specific process so that x' may be estimated. From x' the amount of substance released can then be calculated if the mass of each phase is known.

Example 4. Release Estimate for Container Unloading

Although this unit operation is carried out routinely there is a lack of information on residual material left in the container (drum, can, etc.). Based on industrial experience, a range of 0.1% to 1% based on the container volume was chosen as a reasonable consensus figure. Experimental verification and generation of additional data to relate the release estimate to type of container, mode of unloading and material properties (e.g., viscosity) are in progress.

CONCLUSION

It is recognized that these models and predictive methodologies and the theories provide only order of magnitude estimates and are not a substitute for actual data. They are only as good as the data base from which they were derived. The research needs for this area are enormous for both industry and government, and the Agency is supporting a variety of projects to improve and expand the applicability of this approach. Continued research in this area by EPA and others will no doubt provide great advancement in the future.

REFERENCES

Berman, D.W. 1982. Methods for Estimating Workplace Exposure to PMN Substances. Clement Associates, Arlington, VA. EPA Contract No. 68-01-6065. U. S. Environmental Protection Agency, Office of Toxic Substances, Washington, D.C.

Bomberger, D.C., et al. 1983. Industrial Process Profiles to Support PMN Review: Filling of Drums and Bags. SRI International, Inc., Menlo Park, CA. EPA Contract No. 68-01-6016. Technical Directive 69. U. S. Environmental Protection Agency, Office of Toxic Substances, Washington, D.C.

Clement Associates, Inc. 1981. Mathematical Models for Estimating Workplace Concentration Levels: A Literature Review. EPA Contract No. 68-01-6065. U. S. Environmental Protection Agency, Office of Toxic Substances, Washington, D.C.

Federal Register. 1983. Premanufacture Notice Requirements and Review Procedures; Final Rule and Notice Form. Vol. 48, No. 94, Part II, 40 CFR Part 720. May 13, 1983.

Groggins, P.H. 1935. Unit Processes in Organic Syntheses. 1st ed., McGraw-Hill, New York, New York.

Harris, R.L. and Arp, E.W. 1979. The Emission Inventory. In: Cralley and Cralley (ed.), Patty's Industrial Hygiene and Toxicity, Vol. 3, Chapter 3, John Wiley, New York, New York.

JACA Corporation. 1985. Preliminary Assessment of Predictive Techniques for Estimating Releases and Exposures from Unit Operations. A series of internal reports conducted under EPA Contract No. 68-03-3186. U. S. Environmental Protection Agency, Office of Research and Development, Cincinnati, Ohio.

Lyman, W. J. et al. 1985. Handbook of Chemical Property Estimation Methods. McGraw-Hill, New York, New York.

Midwest Research Institute. 1985. Occupational Exposure Assessment. Draft Final Report, EPA Contract No. 68-02-3930, Work Assignment No. 10. U. S. Environmental Protection Agency, Office of Toxic Substances, Washington, D.C.

The MITRE Corporation. 1985. Potential for Worker Exposure to Chemicals and Release of Chemicals to the Environment in Selected Operations. Draft Report, EPA Contract No. 68-01-6610. U. S. Environmental Protection Agency, Office of Toxic Substances, Washington, D.C.

Office of Technology Assessment, U. S. Congress. 1983. The Information Content of Premanufacture Notices - Background Paper. U.S. Congress, Washington, D.C.

Perry, R.H. and Chilton, C.H. 1963. Chemical Engineers' Handbook, Chapter 4, 4th ed. McGraw-Hill Book Co., New York, New York.

Reynolds, T.S. 1984. Seventy-Five Years of Progress - A History of the American Institute of Chemical Engineers, 1908-1983. American Institute of Chemical Engineers, New York, New York.

U. S. Environmental Protection Agency. 1984. Toxic Substances Control Act (TSCA) Report to Congress. U. S. Environmental Protection Agency, Washington, D.C.

U.S. Environmental Protection Agency. 1985. Engineering Assessment Manual. Chemical Engineering Branch, Economics and Technology Division, Office of Toxic Substances, Washington, D.C.

Weaver, M.A. 1978. Unpublished Data.

Versar, Inc. 1984. Experimental Assessment for Retention of Chemical Liquids on Hands. Draft Report, EPA Contract No. 68-01-6271. U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, D.C.

Wong, K.F. 1982. Unpublished Data.

Wong, K.F. 1984. Exposure to N-Nitrosodiethanolamine in Machine Shops. U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, D.C.